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journal or publication title	Analytica Chimica Acta
volume	680
number	1-2
page range	21-25
year	2010-11-08
URL	http://hdl.handle.net/2297/25774

doi: 10.1016/j.aca.2010.09.031

**An 8-sulfonamidoquinoline derivative having imidazolium unit as an extraction
reagent for use in ionic liquid chelate extraction system**

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Abstract

To evaluate the superiority of using a task-specific onium salt (TSOS), a novel TSOS reagent 1-methyl-3-[2-(8-quinolinylaminosulfonyl)ethyl]imidazolium chloride (HmimesqCl) was synthesized, and its performance in extraction of different divalent metal cations was investigated. This TSOS reagent has both a cationic imidazolium unit and an anionic (proton-dissociable) complexation unit for the extraction of metal cations into an ionic liquid. In the use of HmimesqCl, relatively high extraction of metals resulted in comparison with the use of its non-imidazolium analogs, without changing the extraction selectivity.

Keywords: Ionic liquids; Chelate extraction, Divalent metal cations;
8-Sulfonamidoquinoline derivative; Task-specific onium salt.

1. Introduction

Ionic liquids (ILs) have attracted much interest as novel solvents [1-16]. They are salts with low melting points ($< 100\text{ }^{\circ}\text{C}$ in general) and are hydrolytically stable. Furthermore, several ILs, such as 1,3-dialkylimidazolium hexafluorophosphates and bis(trifluoromethanesulfonyl)imides, are immiscible with water; therefore, they can be used as extraction solvents for liquid-liquid extraction.

The use of ILs as an extraction phase in solvent extraction was reported for organic materials by Huddleston et al. in 1998 [17] and for metal cations by Dai et al. in 1999 [18]. Many researchers have studied the use of ILs in extraction, and several reviews have been published [19-28].

In metal extraction, the low solubility of extraction reagents into the ILs is a serious disadvantage; low extraction capacity often results [19]. Reagents do not solvate well because many ready-made extraction reagents are optimized for use in normal solvent extraction and most have high solubility in low-polar organic solvents. In other words, the development of novel extraction reagents with high affinity to ILs is an important subject. Thus, several researchers have investigated the possible use of several reagents as extraction reagents in an IL-extraction system [29-35]. These reagents contain both a cationic imidazolium unit and a neutral complexation unit, and they are classified as task-specific ionic liquids (TSILs) or task-specific onium salts (TSOSs). Unfortunately, both the imidazolium units and the complexed parts of the TSOSs have positive charges, which lower complexation stability with the metal cation due to electrostatic repulsion [32]. Namely, these TSOSs often have lower extraction ability than their imidazolium-free analogs that show no repulsion in complexation.

We have investigated the use of anionic (proton-dissociable) complexants, including 8-quinolinol derivatives [36-38], β -diketones [38-44] and

8-sulfonamidoquinoline derivatives [38,45] such as 4-methyl-*N*-(8-quinolinyl)benzenesulfonamide (8-(*p*-toluenesulfonamido)quinoline, Htsq), in the IL-extraction. In this system, named the “ionic liquid chelate extraction system”, complexation of the reagents to the metals neutralizes the positive charge of the metals, resulting in a lower positive, neutral or negative charge. Therefore, TSOSs having both the imidazolium and proton-dissociable complexation units can result in suppression of the electrostatic repulsion mentioned above and enhancement of the extraction of the metal in the IL phase. However, the use of a proton-dissociable TSOS has received limited study. To date, only Ouadi et al. [46] has reported on the nature of 1-butyl-3-[3-(2-hydroxybenzylamino)propyl]imidazolium salts as extraction reagents for americium (III); unfortunately, the 2-hydroxybenzylamine unit had limited ability to complex.

In this study, we performed a one-pot synthesis to form a proton-dissociable TSOS containing an 8-sulfonamidoquinoline complexation unit, 1-methyl-3-[2-(8-quinolinylaminosulfonyl)ethyl]imidazolium chloride (8-{2-[1-(3-methylimidazolio)]ethanesulfonamido}quinoline chloride, HmimesqCl; see Fig. 1 (a)). We also displayed its possible use for the extraction of different divalent metal cations into an IL, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]). The 8-sulfonamidoquinoline unit was selected due to the high metal extractability of various other known 8-sulfonamidoquinoline derivatives [38,45,47-57]. When compared to a simple derivative, 8-quinolinylaminosulfonylethane (8-ethanesulfonamidoquinoline, Hesq; see Fig. 1 (b)), the HmimesqCl showed higher extractability for these metals in the IL-extraction system.

2. Experimental

2.1. Reagents

The one-pot synthesis of HmimesqCl was performed as follows: To 100 cm³ of CH₃CN solution containing 1.73 g (12 mmol) of 8-aminoquinoline and 2.9 cm³ (37 mmol) of 1-methylimidazole, 40 cm³ of CH₃CN solution containing 1.2 cm³ (11 mmol) of 2-chloroethanesulfonyl chloride was added dropwise. The mixture was stirred at 50 °C for 5 h after which it was stirred at room temperature overnight. The resulted solid was filtered and colorless needles were obtained after recrystallization from ethyl acetate – methanol. Yield: 1.93 g (5.5 mmol, 50 %), Anal. calcd. for C₁₅H₁₇ClN₄O₂S: C 51.06, H 4.86, N 15.88. Found: C 50.58, H 4.90, N 15.86. ¹H NMR (DMSO-*d*₆): δ = 3.80 (s, 3H, CH₃-), 3.94 (t, 2H, -NHSO₂-CH₂CH₂-), 4.75 (t, 2H, -NHSO₂-CH₂CH₂-), 7.59–7.73 (m, 4H, Ar), 7.80–7.85 (m, 2H, Ar), 8.47 (d, 1H, Ar), 8.97–9.01 (m, 1H, Ar), 9.26 (s, 1H, Ar), 9.96 (br s, 1H, -NHSO₂-).

The synthesis of Hesq was performed from 8-aminoquinoline and 1-ethanesulfonyl chloride using the reported procedure for the preparation of Htsq [58]. ¹H NMR (DMSO-*d*₆): δ = 1.21 (t, 3H, CH₃-), 3.25 (q, 2H, -CH₂-), 7.54–7.77 (m, 4H, Ar), 8.42–8.46 (m, 1H, Ar), 8.93–8.96 (m, 1H, Ar), 9.30 (br s, 1H, -NHSO₂-).

The IL [bmim][PF₆] was synthesized from 1-chlorobutane, 1-methylimidazole and hexafluorophosphoric acid according to reported procedure [17]. Metal standard solutions for atomic absorption spectrometry (1,000 µg cm⁻³ dissolved in dil. nitric acid) were used as metal standards. Other chemicals included reagent-grade materials, which were used without further purification. Distilled deionized water was used throughout.

2.2. Apparatus

A Hitachi model Z-6100 polarized Zeeman atomic absorption spectrophotometer

was used for the determination of the concentration of the metals in the aqueous phase. A Horiba model F-52 pH meter equipped with a Horiba 9678-10D combined glass electrode was used to determine the pH values. The absorption spectra of solutions were recorded on a JASCO V-570 UV/visible/near-infrared spectrophotometer using 1 cm matched quartz cells.

2.3. Distribution of the extraction reagents

Distribution of the extraction reagents between the [bmim][PF₆] and aqueous phases was measured as follows: In a centrifuge tube, an aliquot (10 cm³) of aqueous solution containing 5×10⁻⁴ mol dm⁻³ of each reagent, 1×10⁻¹ mol dm⁻³ of sodium chloride, 1×10⁻² mol dm⁻³ of buffer (chloroacetic acid, acetic acid, 2-(*N*-morpholino)ethanesulfonic acid, 3-(*N*-morpholino)propanesulfonic acid, *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid or *N*-cyclohexyl-2-aminoethanesulfonic acid) and an appropriate amount of NaOH and 1 cm³ of [bmim][PF₆] were shaken at 25±1 °C to be equilibrated. After the two phases were separated by centrifugation, the pH in the aqueous phase was determined, and the measured pH was used as the equilibrated pH. To the aqueous phase, a small amount of concentrated hydrochloric acid was added to acidify to ca. 1 mol dm⁻³ HCl. From the [bmim][PF₆] phase, a small amount was dissolved into 1 mol dm⁻³ HCl. Absorbance of each the solution at 315 nm (maximum absorption wavelength for H₂mimesq²⁺; see below) was measured, and the distribution ratio was calculated.

2.4. Distribution of the metals

In a centrifuge tube, an aliquot (1 cm³) of [bmim][PF₆] containing 1×10⁻³ mol dm⁻³ of HmimesqCl or Hesq and 5 cm³ of an aqueous phase containing 1×10⁻⁵ – 1×10⁻⁴

mol dm⁻³ of M²⁺ (M = Co, Cu, Zn or Cd), 1×10⁻¹ mol dm⁻³ of potassium nitrate, 1×10⁻² mol dm⁻³ of buffer (chloroacetic acid, acetic acid, 2-(*N*-morpholino)ethanesulfonic acid, 3-(*N*-morpholino)propanesulfonic acid, *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid or *N*-cyclohexyl-2-aminoethanesulfonic acid) and an appropriate amount of NaOH were shaken at 25±1 °C for 45 min. After the two phases were separated by centrifugation, the pH and the metal concentration in the aqueous phase were determined. The measured pH was used for numerical analysis as equilibrated pH. The metal concentration in the extraction phase ([bmim][PF₆]) was determined after back-extraction into a 10-fold volume of 1 mol dm⁻³ nitric acid. The extraction ratio (%*E*) of the metal was calculated as 100 × (extracted amount of the metal) / (initial amount of the metal in the aqueous phase), and the distribution ratio (*D*) was calculated as (total metal concentration in the extraction phase) / (total metal concentration in the aqueous phase).

3. Results and discussion

3.1. Acid dissociation equilibria of the reagents

The reagent HmimesqCl dissociates in aqueous solution to Hmimesq⁺ and Cl⁻. The Hmimesq⁺ can show the following acid dissociation equilibria:



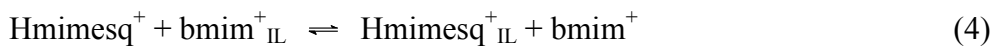
where Eq. (1) corresponds to the acid dissociation of the quinolinium–NH⁺ and Eq. (2) corresponds to that of the sulfonamide–NH. To evaluate these equilibria and to determine respective acid dissociation constants, absorption spectra of 1.0×10⁻⁴ mol dm⁻³ HmimesqCl aqueous solutions containing 1.0×10⁻¹ mol dm⁻³ sodium chloride were measured at different pHs. Some of the spectra are shown in Fig. 2. The two

isobestic points at 294 nm and 319 nm correspond to Eqs. (1) and (2), respectively. Maximum absorption wavelengths and molar absorptivities for $\text{H}_2\text{mimesq}^{2+}$, Hmimesq^+ and mimesq were estimated to be 315 nm for $6.5 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, 304 nm for $3.5 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and 342 nm for $3.5 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively. Furthermore, the acid dissociation constants were obtained as $K_{a1} = 10^{-2.82 \pm 0.01}$ and $K_{a2} = 10^{-7.60 \pm 0.01}$ from the non-linear least-squares fitting of absorbance (at 315 and 342 nm) versus pH. These constants were also determined for Hesq were obtained through the same technique ($K_{a1} = 10^{-3.41 \pm 0.01}$ and $K_{a2} = 10^{-9.01 \pm 0.01}$).

3.2. Distribution of the extraction reagents

It is well known that not only neutral species but also charged species are extractable into a hydrophobic IL phase from an aqueous phase [17]. Consequently, IL/water distribution behavior of extraction reagents can be complicated. Fig. 3 shows aqueous phase pH dependency of the distribution ratio (D_R) between the $[\text{bmim}][\text{PF}_6]$ phase and the aqueous phase for HmimesqCl and Hesq .

The three plateaus in Fig. 3 (a) correspond to the following equilibria:



where subscript IL denotes the $[\text{bmim}][\text{PF}_6]$ phase. The cation-exchange distribution equilibrium constants (K_{CED}) for Eqs. (3) and (4) can be expressed as follows:

$$K_{\text{CED}}(\text{H}_2\text{mimesq}^{2+}) = [\text{H}_2\text{mimesq}^{2+}]_{\text{IL}} [\text{bmim}^+]^2 / [\text{H}_2\text{mimesq}^{2+}] [\text{bmim}^+]_{\text{IL}}^2 \quad (6)$$

$$K_{\text{CED}}(\text{Hmimesq}^+) = [\text{Hmimesq}^+]_{\text{IL}} [\text{bmim}^+] / [\text{Hmimesq}^+] [\text{bmim}^+]_{\text{IL}} \quad (7)$$

In these cases, the $[\text{bmim}^+]_{\text{IL}}$ and $[\text{bmim}^+]$ values are regarded as constant (the aqueous phase is saturated with $[\text{bmim}][\text{PF}_6]$ salt), and the following values (e.g. apparent

distribution coefficients, K_D') are also considered constant:

$$K_D'(\text{H}_2\text{mimesq}^{2+}) = [\text{H}_2\text{mimesq}^{2+}]_{\text{IL}} / [\text{H}_2\text{mimesq}^{2+}]$$

$$= K_{\text{CED}}(\text{H}_2\text{mimesq}^{2+})[\text{bmim}^+]_{\text{IL}}^2 / [\text{bmim}^+]^2 \quad (8)$$

$$K_D'(\text{Hmimesq}^+) = [\text{Hmimesq}^+]_{\text{IL}} / [\text{Hmimesq}^+]$$

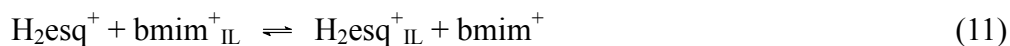
$$= K_{\text{CED}}(\text{Hmimesq}^+)[\text{bmim}^+]_{\text{IL}} / [\text{bmim}^+] \quad (9)$$

Furthermore, the distribution constant (K_D) for neutral mimesq (Eq. (5)) can be expressed as follows:

$$K_D(\text{mimesq}) = [\text{mimesq}]_{\text{IL}} / [\text{mimesq}] \quad (10)$$

By using a non-linear least-squares fitting, the values of $\log K_D'(\text{H}_2\text{mimesq}^{2+})$, $\log K_D'(\text{Hmimesq}^+)$ and $\log K_D(\text{mimesq})$ were determined as 0.71 ± 0.07 , 2.82 ± 0.06 and 0.04 ± 0.01 , respectively.

In the same manner, the two plateaus in Fig. 3 (b) corresponds to the following two equilibria and constants:



$$K_{\text{CED}}(\text{H}_2\text{esq}^+) = [\text{H}_2\text{esq}^+]_{\text{IL}}[\text{bmim}^+] / [\text{H}_2\text{esq}^+][\text{bmim}^+]_{\text{IL}} \quad (12)$$

$$K_D'(\text{H}_2\text{esq}^+) = [\text{H}_2\text{esq}^+]_{\text{IL}} / [\text{H}_2\text{esq}^+]$$

$$= K_{\text{CED}}(\text{H}_2\text{esq}^+)[\text{bmim}^+]_{\text{IL}} / [\text{bmim}^+] \quad (13)$$



$$K_D(\text{Hesq}) = [\text{Hesq}]_{\text{IL}} / [\text{Hesq}] \quad (15)$$

The values of $\log K_D'(\text{H}_2\text{esq}^+)$ and $\log K_D(\text{Hesq})$ were determined as 0.43 ± 0.04 and 2.84 ± 0.01 , respectively. (The distribution of esq^- into the IL phase was not observed.)

It is interesting to note that the values of $K_D'(\text{Hmimesq}^+)$ and $K_D(\text{Hesq})$ are similar to one another regardless of their different electric charges. This fact suggests that introduction of the cationic imidazolium unit to Hesq not only enhanced the hydrophilicity through its positive charge but also maintained IL-philicity because of its

structural similarity to Hesq.

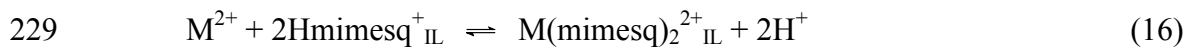
3.3. Extraction behavior of M^{2+}

The %*E* values of M^{2+} into the [bmim][PF₆] extraction phase were plotted as a function of aqueous phase pH (equilibrated pH). The results are shown in Fig. 4. When using HmimesqCl as the extraction reagent, > 95 % of the reagent existed as Hmimesq⁺ in the [bmim][PF₆] phase at pH > ca. 2.8 as shown in Section 3.2 and “Hmimesq⁺” will replace the use of “HmimesqCl” hereafter. Alternatively, > 95 % of Hesq existed as the neutral form in the IL phase at pH > ca. 3.0. The %*E* values, calculated from each metal concentration in the back-extracted solution, were compatible with the metal concentration remaining in the equilibrated aqueous phase. Thus, it was confirmed that the back-extraction using 1 mol dm⁻³ nitric acid was effective not only with the Hesq system but also with the Hmimesq⁺ system.

For all of the M^{2+} s, Hmimesq⁺ showed higher extractability than its imidazolium-free analog Hesq. On the other hand, these two systems showed similar extraction selectivity ($Cu^{2+} > Zn^{2+} > Cd^{2+} \approx Co^{2+}$) as shown in Fig. 4. Namely, the introduction of the imidazolium unit to the Hesq resulted in the enhancement of its extraction performance.

On a side note, Mn^{2+} was not able to be extracted in the examined extraction conditions, and the extraction of Ni^{2+} needed more time to reach equilibration as was reported previously in the use of other 8-sulfonamidoquinoline derivatives [45,54].

When most 8-sulfonamidoquinoline derivatives extract M^{2+} into the [bmim][PF₆] phase, as neutral 1:2 complex has been reported to result [45]. Therefore, by using Hmimesq⁺, the extraction equilibrium and the extraction constant (K_{ex}) can be expressed as follows:



$$K_{ex} = [M(mimesq)_2^{2+}]_{IL} [H^+]^2 / [M^{2+}] [Hmimesq^+]_{IL}^2 \quad (17)$$

In these cases, the D for M^{2+} is expressed as follows:

$$\begin{aligned} D &= [M(mimesq)_2]_{IL} / ([M^{2+}] + [M(OH)^+] + [M(OH)_2]) \\ &= ([M(mimesq)_2]_{IL} / [M^{2+}]) (1 + \beta_1[OH^-] + \beta_2[OH^-]^2)^{-1} \\ &= (K_{ex}[Hmimesq^+]_{IL}^2 / [H^+]^2) (1 + \beta_1[OH^-] + \beta_2[OH^-]^2)^{-1} \end{aligned} \quad (18)$$

where β_1 and β_2 are stability constants for hydroxo complexes of $M(OH)^+$ and $M(OH)_2$, respectively. Assumingly, the following approximate relationship can be true:

$$\begin{aligned} \log D(1 + \beta_1[OH^-] + \beta_2[OH^-]^2) \\ = \log K_{ex} + 2 \log C(HmimesqCl)_{IL} + 2pH \end{aligned} \quad (19)$$

where $C(HmimesqCl)_{IL}$ is the initial concentration of $HmimesqCl$ in the $[bmim][PF_6]$ phase.

To confirm the extracted species and the extraction equilibria, the relationships between $\log D(1 + \beta_1[OH^-] + \beta_2[OH^-]^2)$ of M^{2+} and aqueous phase pH at a fixed $C(HmimesqCl)_{IL}$ and between the $\log D(1 + \beta_1[OH^-] + \beta_2[OH^-]^2)$ and $\log C(HmimesqCl)_{IL}$ at fixed pH (equilibrated pH) were determined. The following β_i values for Co^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} were used for the calculation: $\log \beta_1 = 4.35, 6.30, 5.04$ and 3.92 , and $\log \beta_2 = 9.19, 10.70, 11.09$ and 7.64 , respectively [59]. The obtained plots are shown in Figs. 5 and 6, respectively. In all cases, the plots formed straight lines with slopes close to 2. Based on these plots, the extraction mechanism for M^{2+} must be expressed as Eq. (16) for the $Hmimesq^+$ system.

The $\log K_{ex}$ values in the $Hmimesq^+$ system were calculated from experimental data ($pH > 2.8$) using Eq. (19). The obtained values are shown in Table 1 alongside those of the $Hesq$ and $Htsq$ [45] systems. The $\log K_{ex}$ values in the $Hmimesq^+$ system were 1.3 – 2.3 higher than those in the $Hesq$ system, which correspond to 0.7 – 1.2 pH

units in the %*E* vs. pH plots. Furthermore, these values were higher than those of the more hydrophobic Htsq. From these facts, it can be deduced that the use of a TSOS, which has a proton-dissociable complexation (chelation) group, as an extraction reagent in the IL-extraction system is effective for the high-performance extraction of metal cations in the IL phase.

While the solubility of Hesq in [bmim][PF₆] was ca. 10⁻² mol dm⁻³, HmimesqCl dissolved in [bmim][PF₆] at more than 1 mol dm⁻³. Because of this higher value, this TSOS possesses a much higher extraction capacity. Furthermore, by adding aqueous sodium hexafluorophosphate to an aqueous solution of HmimesqCl, a phase separation was brought about. The newly formed viscous lower phase, probably [Hmimesq][PF₆], may be a hydrophobic IL, but further detailed investigation concerning the species is required.

Acknowledgment

This study was financially supported in part by a Grant-in-Aid for Scientific Research (Nos. 21550075 (to H. I.) and 22550071 (to N. H.)) from the Japan Society for the Promotion of Science, and the Asahi Glass Foundation (to Ko. M.).

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Figure/Table legends

Fig. 1 Chemical structures of HmimesqCl (a) and Hesq (b).

Fig. 2 Absorption spectra of the 1.0×10^{-4} mol dm⁻³ HmimesqCl aqueous solutions containing 1.0×10^{-1} mol dm⁻³ sodium chloride at different pH conditions (0.93, 2.26, 2.66, 3.05, 3.81, 4.69, 6.95, 7.44, 7.96, 8.63 and 11.29).

Fig. 3 Relationship between logarithmic distribution ratio ($\log D_R$) for extraction reagents and aqueous phase pH. Initial reagent concentration in the aqueous phase was 5.0×10^{-4} mol dm⁻³. The solid curves were obtained by a non-linear least squares fitting. Reagent: (a) HmimesqCl, (b) Hesq.

Fig. 4 Plots of the extracted ratios (% E) for some divalent metals as a function of the aqueous phase pH equilibrated with extraction phase in the Hmimesq⁺ (a) and Hesq (b) systems. Initial reagent concentration in the [bmim][PF₆] phase was 1×10^{-3} mol dm⁻³. Sample: (\blacklozenge) Co²⁺, (\blacksquare) Cu²⁺, (\bullet) Zn²⁺, (\blacktriangle) Cd²⁺.

Fig. 5 Plots of the $\log D(1 + \beta_1[\text{OH}^-] + \beta_2[\text{OH}^-]^2)$ for some divalent metals as a function of the aqueous phase pH in the Hmimesq⁺ system. Initial HmimesqCl concentration in the [bmim][PF₆] phase was 1×10^{-3} mol dm⁻³. The broken line, with a slope of 2, was obtained by a least squares fitting. Sample; (\blacklozenge) Co²⁺, (\blacksquare) Cu²⁺, (\bullet) Zn²⁺, (\blacktriangle) Cd²⁺.

Fig. 6 Plots of the $\log D(1 + \beta_1[\text{OH}^-] + \beta_2[\text{OH}^-]^2)$ for some divalent metals as a

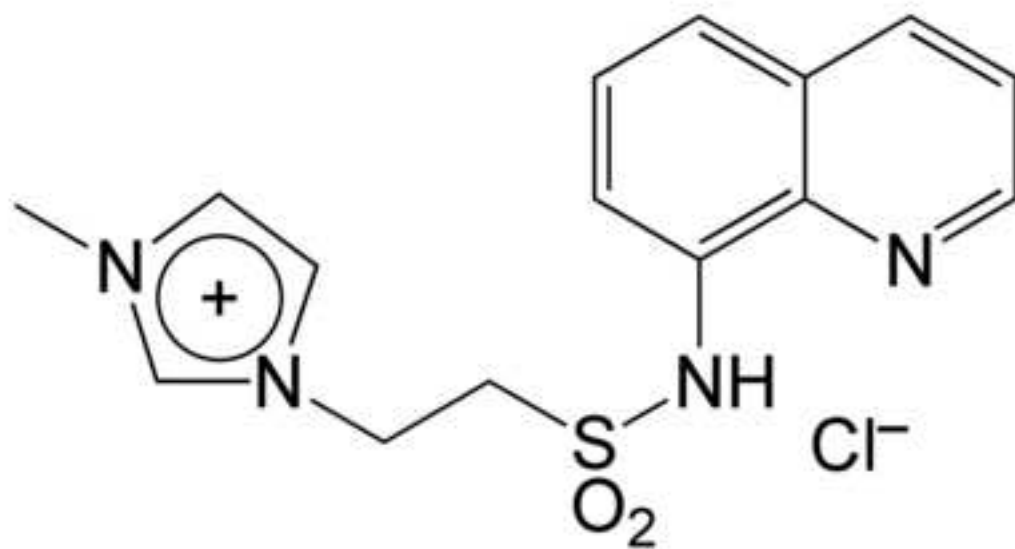
389 function of logarithmic initial concentration of HmimesqCl in the extraction phase.
390 Equilibrated aqueous phase pH was 4.1 (Co^{2+}), 2.6 (Cu^{2+}), 5.0 (Zn^{2+}) and 6.2 (Cd^{2+}).
391 The broken line, with a slope of 2, was obtained by a least squares fitting. Sample: (a)
392 Co^{2+} , (b) Cu^{2+} , (c) Zn^{2+} , (d) Cd^{2+} .
393
394 Table 1 Determined $\log K_{\text{ex}}$ values for the divalent metal cations in the [bmim][PF₆]
395 phase for each of the Hmimesq⁺, Hesq and Htsq systems (25±1 °C)

Table 1 Determined $\log K_{\text{ex}}$ values for the divalent metal cations in the [bmim][PF₆] phase for each of the Hmimesq⁺, Hesq and Htsq systems (25±1 °C)

Cation	Extraction reagent		
	Hmimesq ⁺	Hesq	Htsq [45]
Co ²⁺	−6.12±0.11	−7.95±0.26	−7.54±0.18
Cu ²⁺	1.33±0.13	−0.07±0.12	0.83±0.14
Zn ²⁺	−3.81±0.04	−5.12±0.13	−4.35±0.12
Cd ²⁺	−6.07±0.02	−8.34±0.02	−6.84±0.03

Figure 1
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(a)



(b)

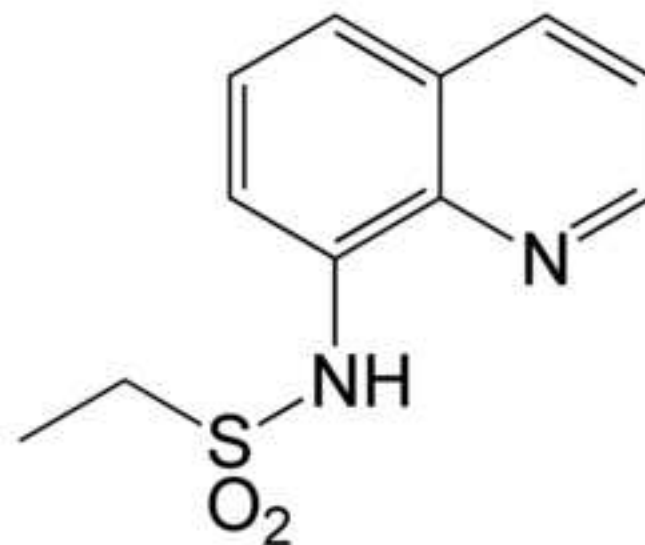


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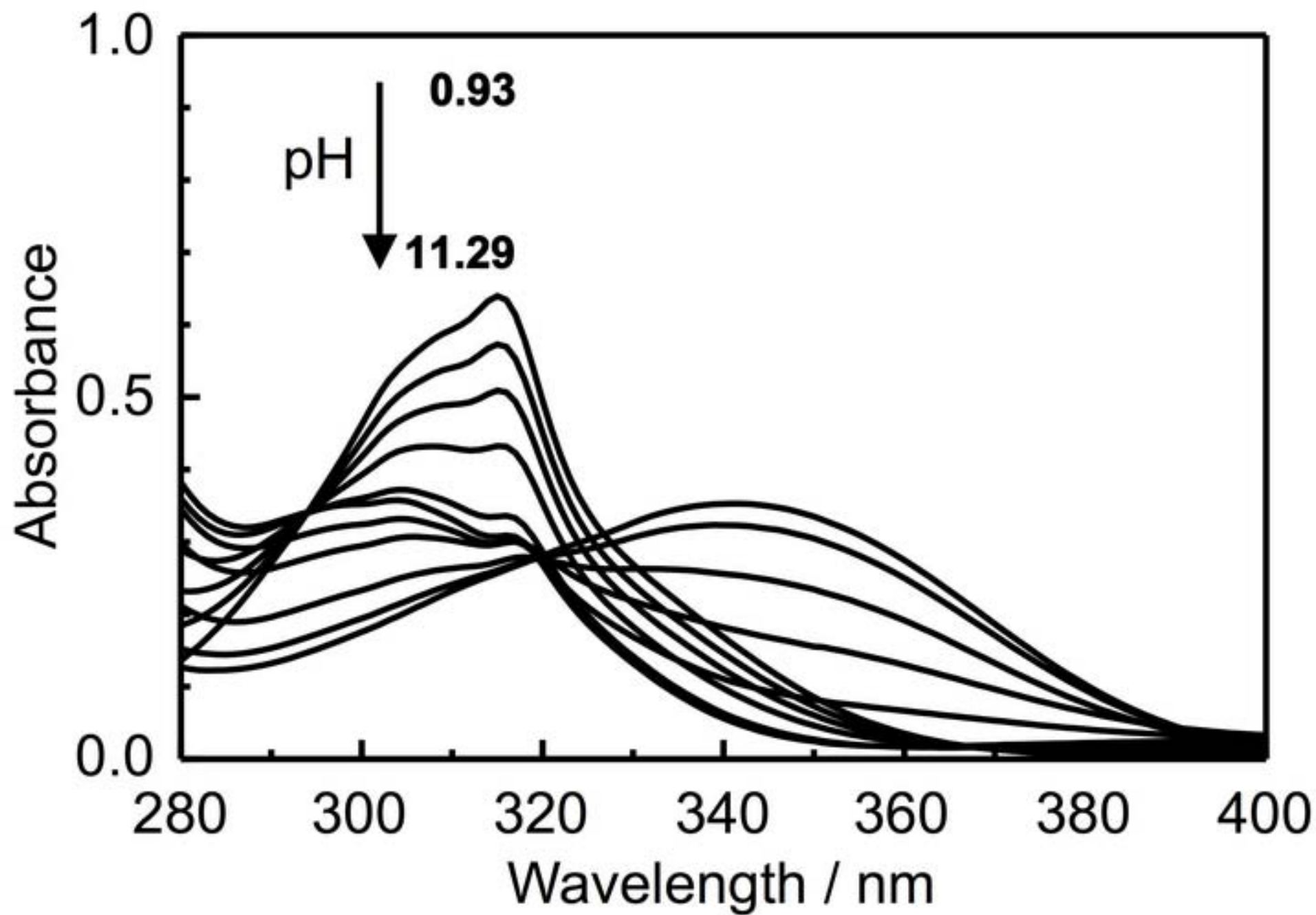


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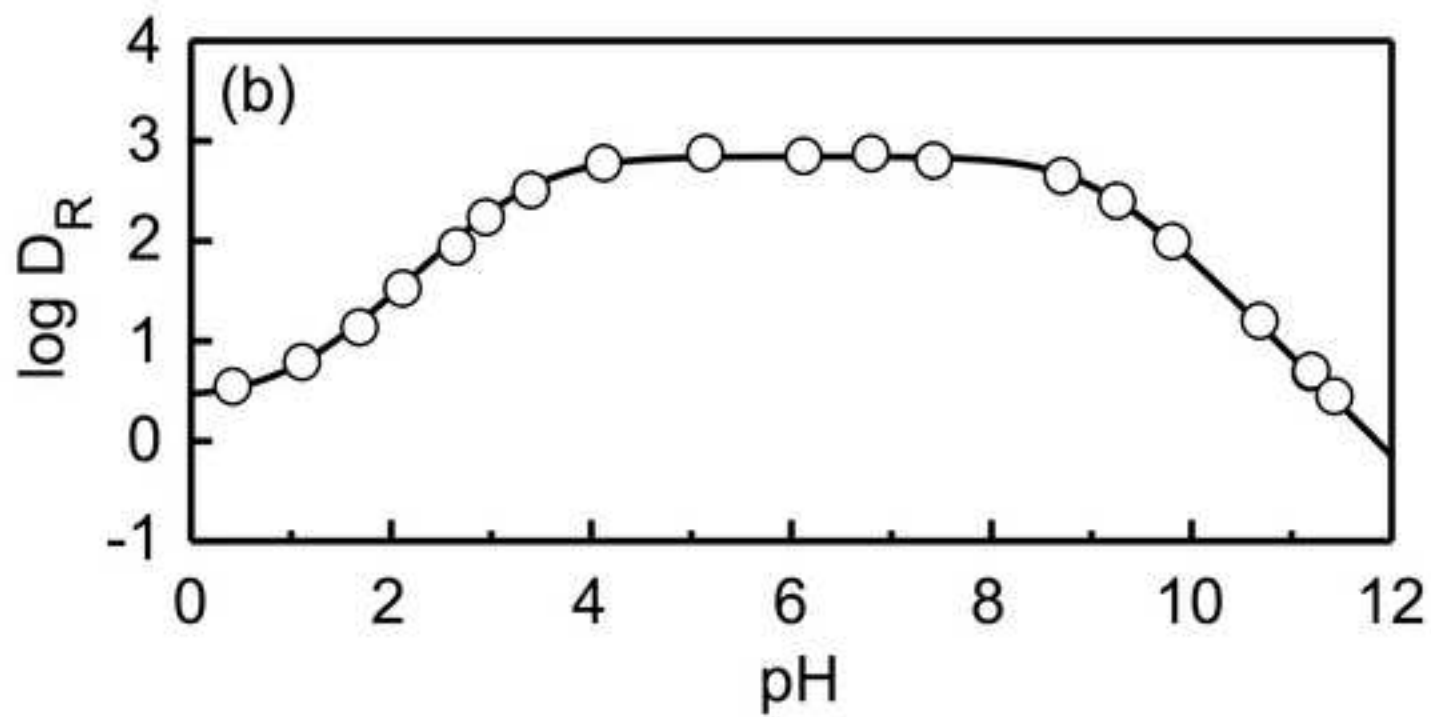
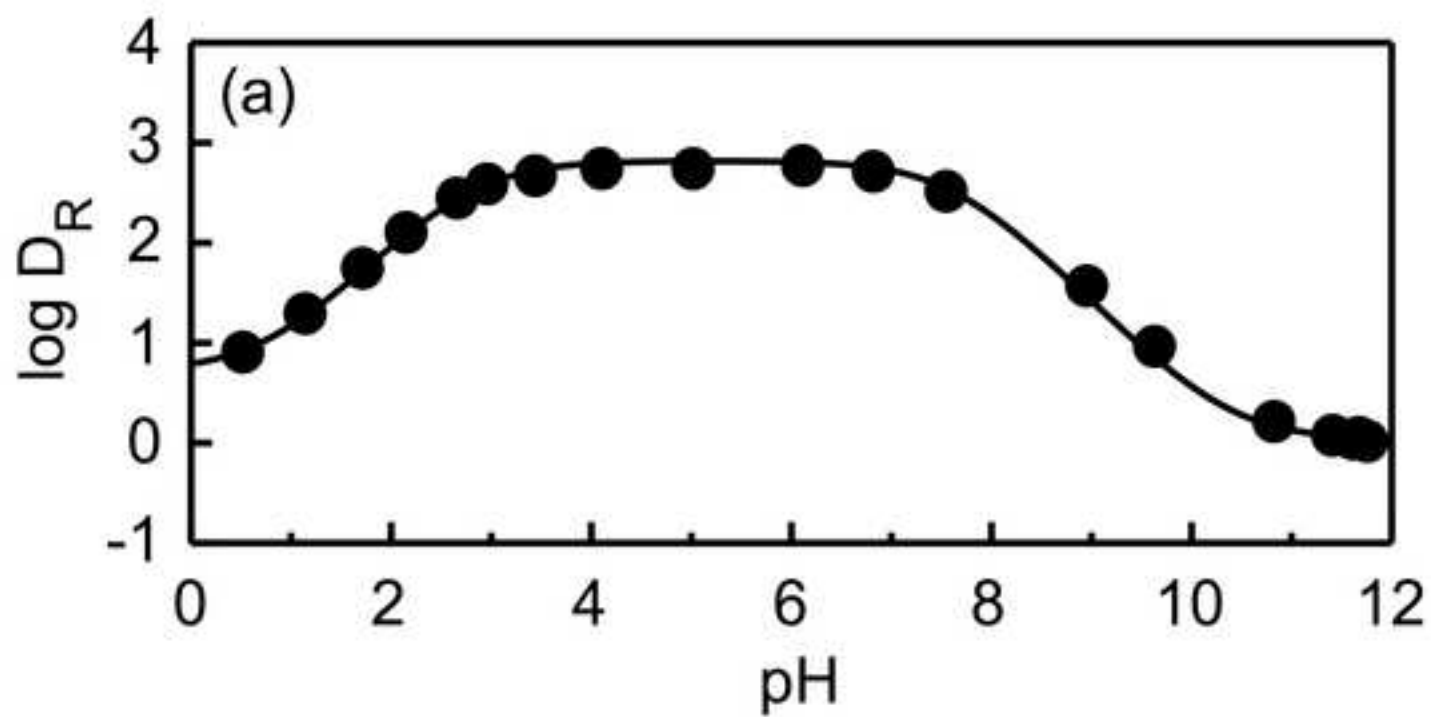


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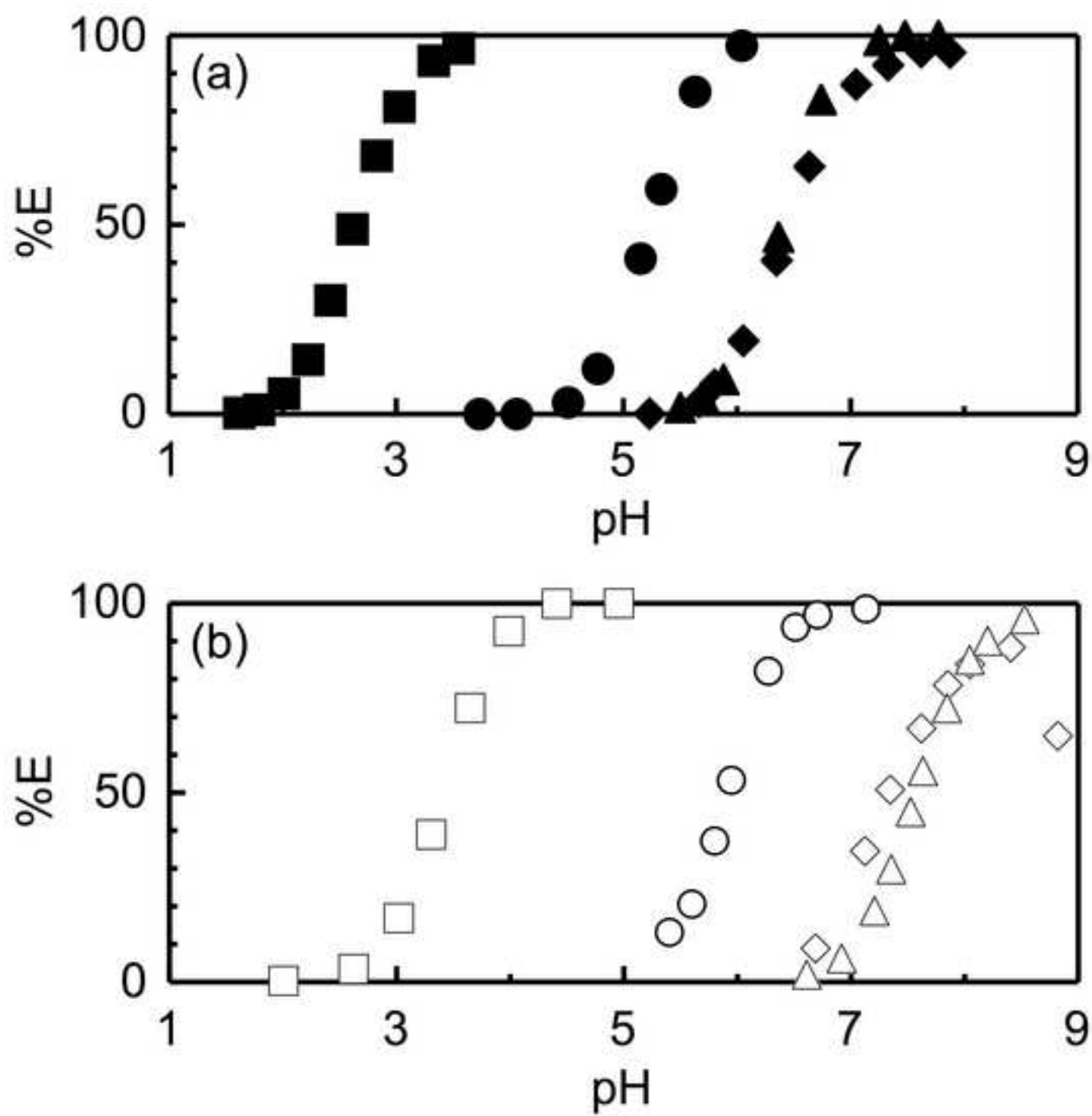


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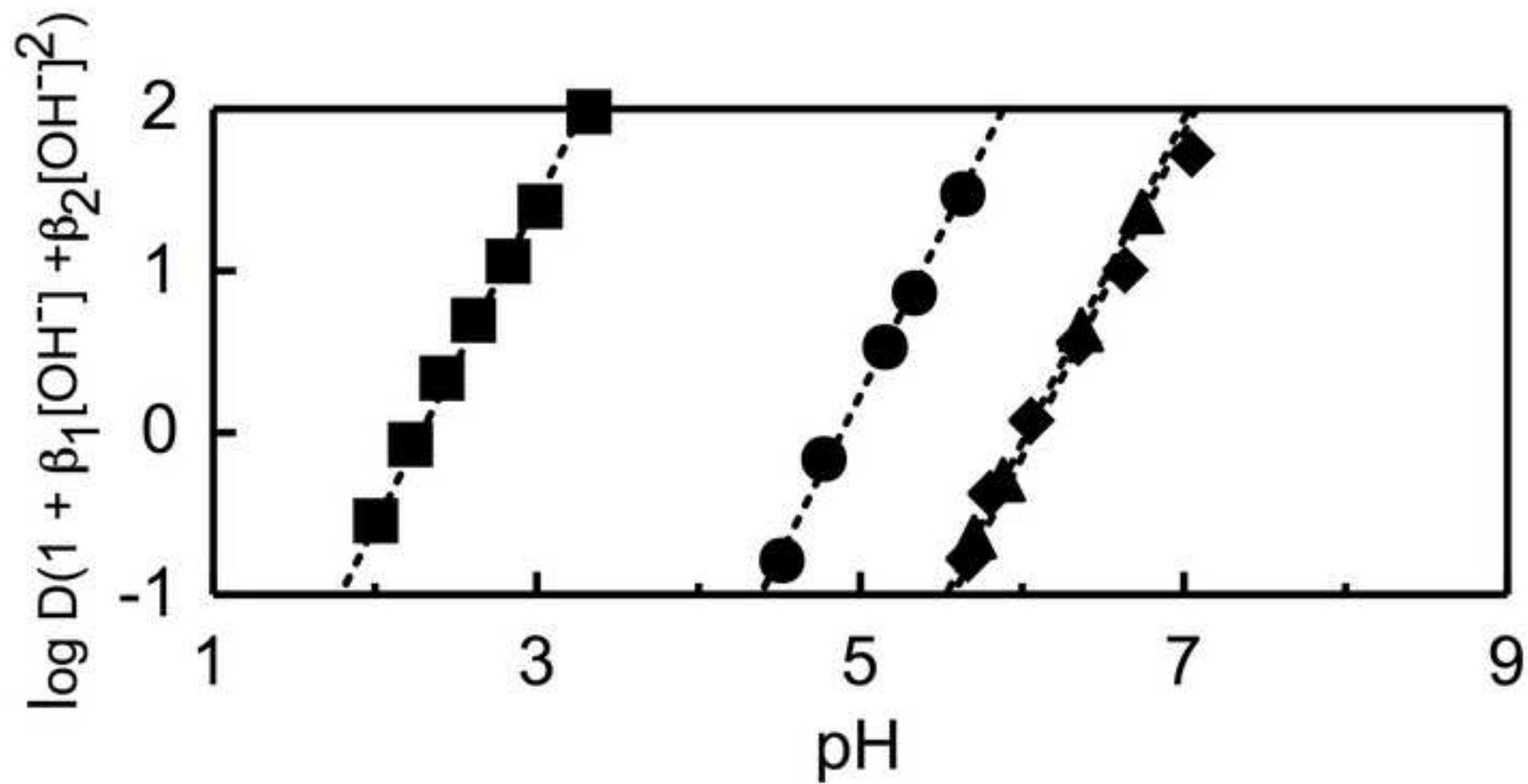


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